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Enhancing Thermal Resilience of Epoxy/Vinylester-MWCNT Nanocomposites

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Abstract: The thermal resilience of composite materials is critical for applications in extreme environments, where stability under high temperatures and oxidative conditions is paramount. This research explores improving the thermal stability and resistance to heat-induced oxidative degradation in epoxy/vinylester matrix composites by reinforcing them with multi-walled carbon nanotubes (MWCNTs). Adding MWCNTs to the polymer matrix notably enhances the nanocomposites' thermal characteristics, such as their degradation temperature and resistance to oxidation. To assess the thermal stability and degradation patterns of these composites under accelerated aging, various experimental methods, including thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were utilized. Results indicate that MWCNTs act as effective reinforcing agents by promoting a more stable cross-linked structure, enhancing the material's ability to resist oxidative degradation at elevated temperatures. The study also examines the effect of different MWCNT loadings on the thermal properties, providing insight into the optimal reinforcement concentration for maximum performance. The findings demonstrate that the epoxy/vinylester-MWCNT nanocomposites offer a promising approach to improving the thermal resilience of polymeric materials for high-performance applications in industries such as aerospace, automotive, and electronics.

Keywords; Thermal resilience; multi-walled carbon nanotubes; thermal stability; polymer nanocomposites; oxidative resistance.

1. Introduction

Recent developments in various fields of biomechanics, astronautics, and aeronautics have produced sophisticated structural materials with exceptional specific characteristics. Carbon nanotube (CNT)-reinforced polymer composites are unique among them because of their exceptional mechanical, thermal, chemical, electrical, and optical characteristics [1-3]. The continuous phase in these nanocomposites is the polymer matrix, which is essential for binding micro- and nanoscale reinforcements. By ensuring structural integrity, enabling uniform stress distribution, and enhancing tensile strength, toughness, and impact resistance, this binding enhances the composite's overall performance [4-5].

In order to provide consistent operation under high-temperature conditions, the polymer matrix is essential for improving thermal stability by preserving dimensional integrity and resistance to temperature changes. Additionally, it improves the barrier qualities of the composite, reducing the accessibility of moisture, gasses, and other materials for enhanced protection. By adding nanoparticles, the composite's mechanical, thermal, and barrier characteristics are further improved, rendering it suitable for cutting-edge uses. The particular functional requirements of the nanocomposite determine which matrix is preferable. Thermosetting polymers, thermoplastic polymers, and elastomers are the three general categories into which polymer matrices fall. Cross-linked molecular structures, which form a stiff, three-dimensional network during the curing or polymerization process, are what define thermosetting polymers. These materials cannot be warmed after they have cured. They could nevertheless maintain their flexibility at high temperatures if the cross-link density is modest [6-7]. In contrast, thermoplastic polymers are produced up of molecules joined by weak intermolecular interactions, like hydrogen or van der Waals bonds, as opposed to long-lasting chemical cross-links. These weak bonds suddenly dissolve under pressure and heat, enabling the molecules to transfer and change shape. These secondary bonds develop as the substance cools, solidifying the molecular structure. The requirements of the particular application, such as operating temperature, exposure to the environment, mechanical performance, and material recyclability, determine which matrix is ideal for nanocomposites [8-9].

Epoxy resins are widely used as matrix materials in high-performance composite systems due to their distinctive molecular structure and flexible processing options [10]. When epoxide groups react with curing chemicals, they undergo ring-opening polymerization, producing strongly crosslinked networks that compose up epoxy resins. The key to their remarkable qualities is this mechanism, which transforms monomers into complex three-dimensional structures [11]. Epoxy systems have variable hardness levels, dimensional stability, and high adhesion before curing [12]. They produce composites that balance low weight with high mechanical strength and stiffness when integrated with reinforcing fibers. Epoxy-based composites are also essential for use in sectors like medical equipment, rail transportation, and aircraft due to their resilience to corrosion and wear [13]. Despite these precautions, epoxy resins remain dominant in numerous industrial applications due to their outstanding performance, versatility in processing, and wide range of uses [14-16].

This article studies the enhanced thermal resilience of epoxy/vinylester-MWCNT nanocomposites against thermo-oxidative degradation.

2. Experimental Details

Diglycidyl ether of bisphenol A (DGEBA), a liquid epoxy resin that comprises for more than 75% of the resin exploited in industrial applications, is the epoxy resin employed in the current research. It is provided below the skill name Araldite® GY 2600, which is a registered brand for the commercial resins manufactured by Huntsman Advanced Materials. Polyamines or their adducts can cure Araldite® GY 2600 to produce solvent-free coatings, flooring screeds, trowelling compounds, etc.
MWCNTs from the NANOCYLTM NC7000 series, which were synthesized using the catalytic carbon vapor deposition (CCVD) method. These are particularly important in applications that require a low electrical separation threshold, such as high-performance electrostatic dissipative coatings. The NC7000 powder is available in quantities ranging from 2 kg to several tonnes, with pre-dispersed forms (PLASTICYLTM, EPOCYLTM, AQUACYLTM) also available.

Synthesis of Epoxy-MWCNTs Nanocomposites: MWCNTs and Epoxy resin were mixed in Table 1 at the weight ratios indicated. In order to spread the MWCNTs, the MWCNTs were first added directly to the molten Epoxy resin and then the blend was combined under a magnetic agitator for 10 minutes at 80°C. When the MWCNTs were properly dispersed, I added the hardener, 14.4 gram of aradur 2958, while stirring, and produced several samples. For the first sample preparation in this example, 80 gm of epoxy resin and 14.4 gm of hardener was applied. Second, the same volume of epoxy resin and hardener has been used; the only variation was indeed the percentage of MWCNTs, which varied between 0.5, 1.0, and 2.0. After that, a casting technique was used to prepare the illustrations with the correct dimensions before the molten sample was allowed to form into the aluminium mould. The sample was then removed out of the mould and left at ambient temperature for 72 hours for post-curing.

Synthesis of Vinyl ester-MWCNTs Nanocomposites: The Fiberbond 701 resin (Ruia Chemical Pvt. Ltd.) Vinyl Ester matrix used in this research was cured with the hardener (catalyst) "MEKP" and Accelerator (cobalt naphthenate). The MWCNTS was used to produce the nanocomposites. Thus far, the MWCNTs have improved the viscosity of the vinyl ester resin. The dispersion technique was modified in order to increase the maximum CNT content and advance the quality of the nanocomposites. Furthermore, the material could no longer be degassed before curing, which resulted in trapped air in the finished composites. Given that the shear forces generated from mixing in the suspension did, in fact, directly affect the viscosity. As mentioned, I used 30 g of vinylester resin and 0.45 gram each of hardener and accelerator respectively as mentioned in Table 1.

Table 1: Specimen Composition.

Sample code	Specimen Composition
1	Epoxy+Hardener+ 0%MWCNT
2	Epoxy+Hardener+0.5%MWCNT
3	Epoxy+Hardener+1% MWCNT
4	Epoxy+Hardener+2% MWCNT
5	Vinylester+Hardener+Accelerator
6	Vinylester+Hardener+Accelerator+0.5% MWCNT
7	Vinylester+Hardener+Accelerator+1%MWCNT
8	Vinylester+Hardener+Accelerator+2%MWCNT

A dynamic mechanical analyzer (TA Q800) was cast-off to examine the dynamic mechanical parameters as a function of temperature, including storage modulus (E'), loss modulus (E''), and loss factor (Tan δ). The virgin PC, TPU, and their blend nanocomposites were examined using DSC Q20 (TA Instruments, USA) is used for Differential Scanning Calorimetry (DSC). The heating rate was set at 1°C/min, and samples weighing 5–10 mg were used. To avoid oxidative deterioration, all DSC tests were carried out in a nitrogen environment at temperatures between 40 and 225 °C. Prior to each DSC test, the baseline was calibrated using empty aluminium pans. The DSC data allowed for the determination of key thermal event temperatures, such as the glass transition temperature. In this study, TGA was conducted on both nanocomposites and their matrix to evaluate the decomposition rates and thermal stability of the samples. X-ray diffraction (XRD) patterns of model powder were obtained using a Rigaku Ultima-III X-ray diffractometer, prepared with a Cu target at 40 kV and 100 mA.

3. Results and Discussion

Differential Scanning Calorimeter Analysis: A Perkin Elmer Pyris differential scanning calorimeter (DSC) was used for the investigations, which were carried out in both dynamic and isothermal modes. During the curing process, the "heat flow" into and out of the epoxy resin is measured by DSC. The glass transition temperature (T_g) of fully cured nanocomposites is also evaluated using it. To guarantee full curing, the samples were heated at a rate of 200°C per minute to a temperature higher than the anticipated T_g and subsequently cooled below T_g. The T_g was calculated using a heating rate of 30 °C per minute with a 10°C change every 60 seconds in the temperature range of 500 °C to 800 °C. It has been noted that MWCNT can have a positive or negative effect on an epoxy system's T_g, depending on the conditions. When polymer chain movement is restricted, an epoxy-MWCNT nanocomposite shows a higher T_g than pure resin due to intercalation within the MWCNT layers. The interaction between the MWCNT and polymer molecules reduces the flexibility of the polymer chains, thereby increasing the Tg. Conversely, adding MWCNT to epoxy resin was found to decrease T_g, likely due to increased segmental mobility within the polymer caused by the reduced cross-linking in the hybrid material.

Table 2: Glass transition temperature (T_g) of Epoxy/Vinylester- MWCNT nanocomposites.

Epoxy + Hardener	Epoxy + Hardener + MWCNT	Vinylester + Hardener + Accelerator	Vinylester + Hardener + Accelerator + Mwcnt
68.70 ℃	87.89 ℃	70.04 ℃	90.23 ℃

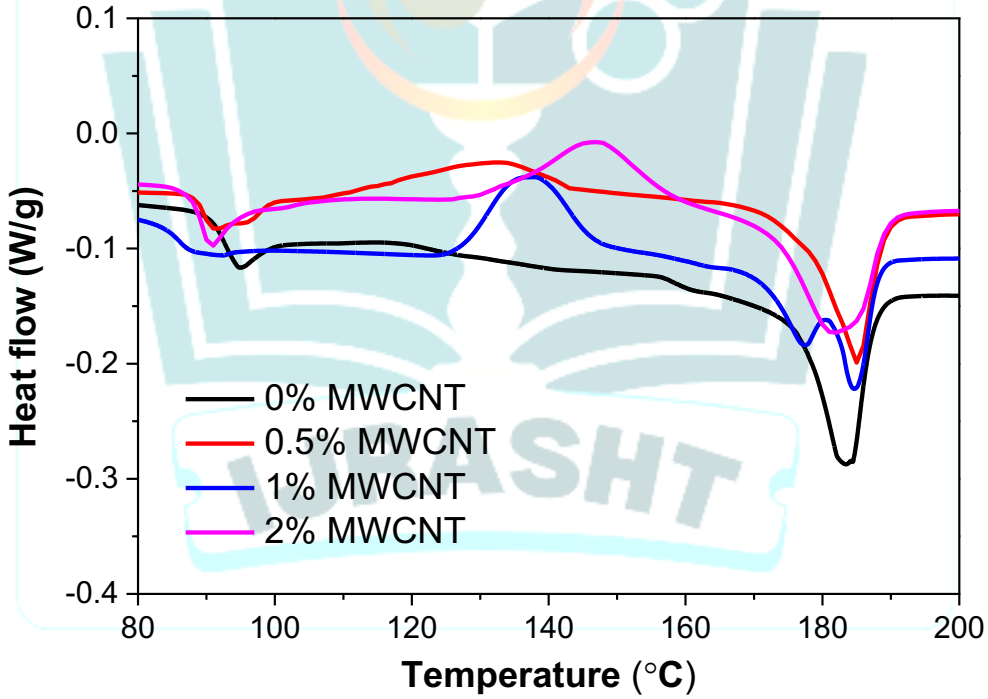

Figure 1: DSC thermogram of epoxy-MWCNTs nanocomposites.

As per numerous studies, MWCNT can both enhance and diminish the T_g of an epoxy system. An epoxy MWCNT nanocomposite's glass transition temperature can be lower than that of the pure resin because of the confinement of the polymer chains (Figures 1 & 2). Intercalation into the layers of the MWCNT is the cause of this. The mobility of the polymer chains is reduced by the contact between the MWCNT and the polymer molecules, increasing the T_g. The absence of certain cross-linking in the hybrid material results in an increase in the partitioned mobility inside the polymer. Table 2 illustrates the relationship between the number of MWCNTs and the glass transition temperature, T_g. Importantly, compared to MWCNT-based composites, which only exhibit slight fluctuations, Vinyl Ester/MWCNTs-based nanocomposite exhibits a greater T_g variation.

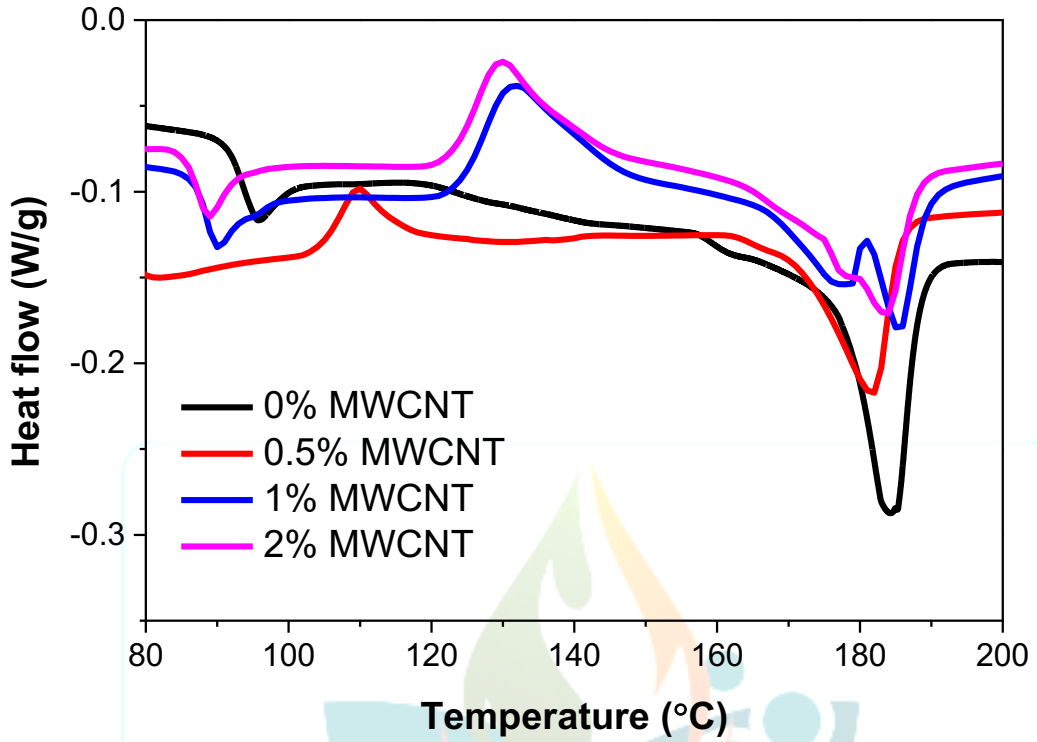

Figure 2: DSC thermogram of vinylester-MWCNTs nanocomposites.

Thermal Gravimetric Analysis (TGA): A Perkin Elmer Pyris 1 thermogravimetric analyser (TGA) was cast-off. The experiments were carried out in dynamic mode, using a continuous heating rate of 20°C/min, on both pure materials and the synthesized nanocomposites, until the resin totally broke down at 800°C. The thermal stability of polymeric materials is usually evaluated by thermogravimetric analysis (TGA), which evaluates the weight loss carried on by the formation of volatile substances during degradation at high temperatures. While non-oxidative degradation occurs when samples are heated without an inert gas flow, oxidative degradation could occur when samples are exposed in an oxygen or air atmosphere. By functioning as a more potent insulator and barrier to the volatile chemicals emitted during decomposition, MWCNT has typically been demonstrated to improve thermal stability.

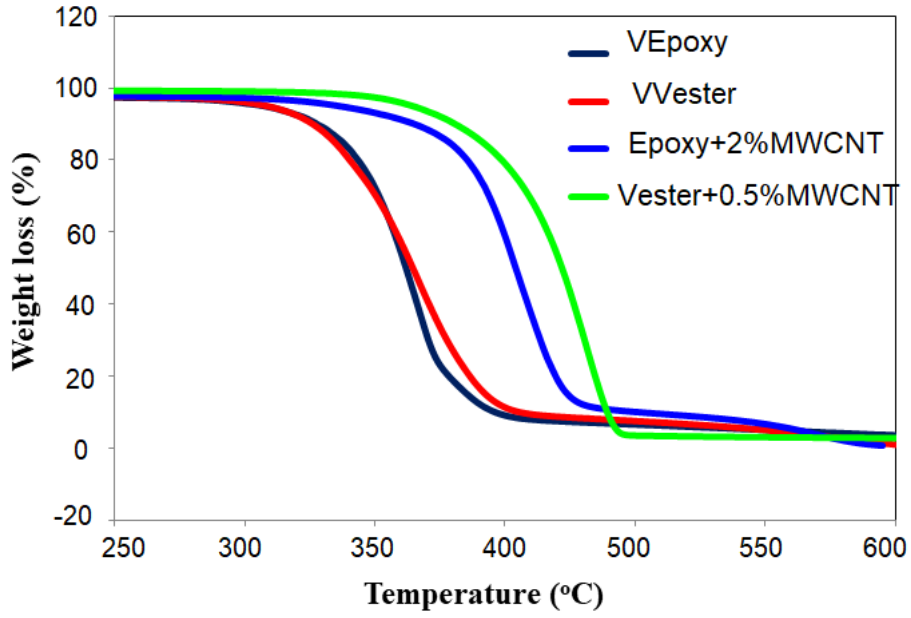

Figure 3: Weight loss% due to heating in presence of N_2.

The thermal degradation of pure epoxy resin in nitrogen results in a 9.006% residue, occurring in two stages with the maximum degradation rate between 50 and 300°C. Water elimination is the initial stage of deterioration, which causes C-C unsaturation's to develop. The allylic bonds between carbon and oxygen in this unsaturated province become the epoxy network's thermally weakest bonds. They breakdown, leading the crosslinked structure to split, efficiently forming pieces that are minor sufficient to evaporate at high temperatures. However, evaporation is confined to 3500 °C because it compares with rearrangements like cyclisation, which produce a rather stable structure that deteriorates in the following phase of degradation. The C-Phenyl bonds of bisphenol-A and other chemical bonds in the epoxy network undergo severe breakdown in this stage, which produces about complete evaporation. Limited recombination to a thermally stable charred results in the formation of a minor fraction of charred residue (4%). 50 to 800 ° C were observed. 5–10 mg was taken as a sample. In comparison to virgin epoxy, which declined by 50% at 402.57°C and left a residue of 9.06, epoxy having 2% MWCNT deteriorated by 414.90% at 800°C and 7.867°C, accordingly (Figure 3). It exhibits an increase in the thermal properties.
In general, it was found that adding MWCNTs to the polymer matrix enhanced heat stability. Pure epoxy resin thermally reduces in nitrogen in a two-step method, with the extreme rate occurring at 301 and 4140° C and a 9.006% residue. Water elimination is the initial stage of breakdown, which enables C-C unsaturation to progress. The allylic linkages connecting carbon and oxygen in this unsaturated area become the epoxy network's thermally weakest bonds. They split down, resulting in parts of the crosslinked structure that are actually small enough to evaporate at high temperatures. Volatilization is limited to 3500°C, though, because it is compared to rearrangements like cyclization, which produce an essentially stable structure that dissolves in the ensuing degradation phase. In this phase, bisphenol-A's C-phenyl linkages and other chemical links in the epoxy network break down significantly, leading to almost total evaporation. Constrained recombination results in the development of a tiny amount of charred residue during decomposition (4%), which is a thermally stable burned substance of reactive degrading kinds.

Table 3: Weight loss% data due to heating in inert atmosphere(N_2).

Sample	T_{onset}	T_{end}	T_{peak}	$T_{10\%}$	$T_{30\%}$	$T_{50\%}$	$T_{90\%}$
Epoxy+ Hardener	302.69	402.64	364.07	361.71	388.83	402.98	600.54
2% MWCNT	307.78	409.85	366.18	362.88	390.74	414.88	610.69
VE+Hardener+Accelerator	309.62	410.43	365.17	357.34	387.45	460.58	479.28
0.5% MWCNT	304.81	406.91	364.67	364.21	389.27	466.93	491.27

Since the idea operate on a microscale, improving stiffness and toughness does not require homogeneously scattered multilayer MWCNT in the epoxy matrix. Even standard composites offer enhanced toughness and tensile modulus. In spite of the MWCNT layers not being exfoliated, composites containing MWCNT modulation have higher moduli and mechanical values than pure epoxy. The multilayer MWCNT's high modulus directly contributes to the composite's increased stiffness. Moreover, the MWCNT particles function as stress concentrators, improving toughness by increasing matrix yield. The insufficient dispersion of MWCNT layers with a large surface area interacting with the matrix at the nanoscale is the cause of the strength decrease. As a result of particle debonding and failure within the larger particles, the tensile strength of all the composites developed is reduced. Thermal strength improvements in the nanocomposites were minimal, as shown by the Tg studies conducted on both the MWCNT and Epoxy/Vinylster-MWCNT nanocomposites. This suggests that the strength could potentially be enhanced with better dispersion.

Dynamic Mechanical Analysis Epoxy Nanocomposite: The glass transition temperature (T_g) and storage moduli of epoxy and epoxy/vinylester-MWCNT nanocomposites were examined using DMA. Table 3 and Figures 1 and 2 provide the information. MWCNT particles were introduced to epoxy matrix, but still no noteworthy changes in T_g were perceived; however, the storage moduli substantially increased with increased MWCNT concentration. The nanocomposite's storage modulus increased with the addition of 2.0 wt% MWCNT. Polymer/MWCNT nanocomposites often exhibit more significant storage modulus increases in the rubbery state as compared to those in the glassy state. This effect is most likely caused by the presence of MWCNT layers with a large surface area and high feature ratio, which act as effective and ideal crosslinkers.

Table 4: Glass-transition temperature and storage moduli of DMA-derived epoxy/closite clay nanocomposites.

Content of MWCNT	Tan (ϱ) (MPa)	Loss modulus (MPa)	T_g (°C)	T_g (°C) Loss
VEpoxy	0.7152	400.3	90.52	77.65
VVester	0.9596	128.6	100.68	84.26
EPOXY+2%MWCNT	0.7274	404.3	104.54	83.35

Vinylester+0.5%MWCNT	1.012	311.4	90.97	71.30

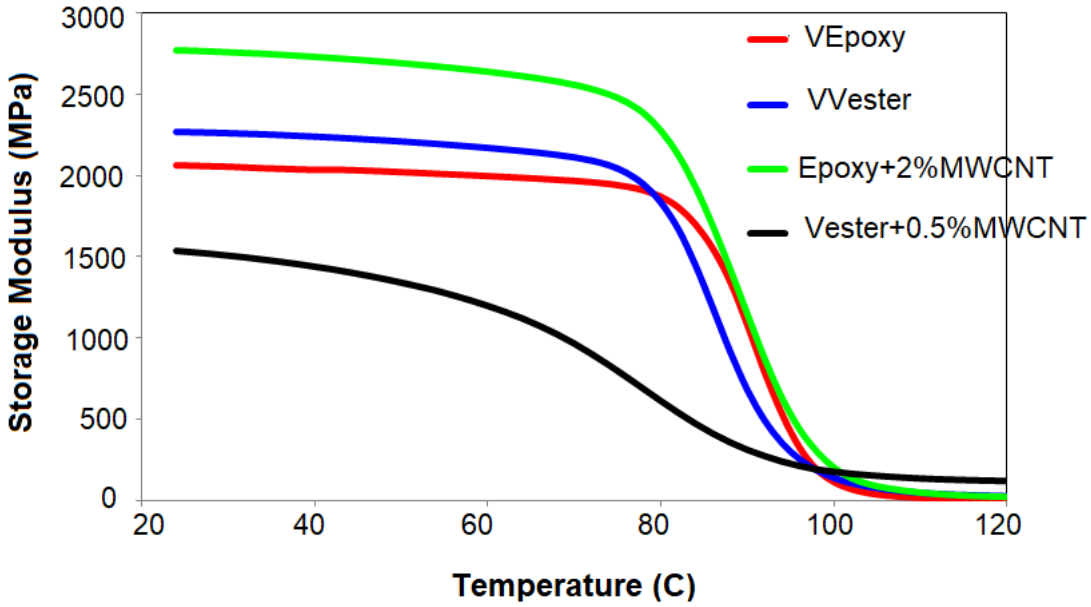

Figure 4: Storage modulus versus temperature for the arranged Epoxy & Epoxy/Vinylester-MWCNT nanocomposites

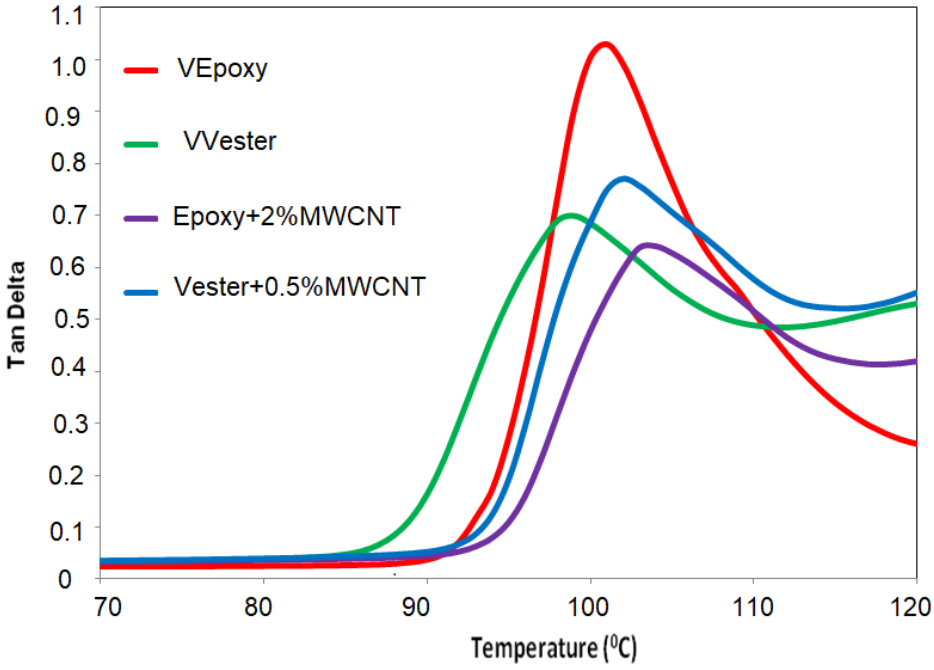

Figure 5: Tan δ versus temperature for the neat Epoxy/Vinylester & the Epoxy2%/Vinylester0.5%MWCNT nanocomposites.

4. Conclusion

The study examined the impact of various MWCNT characteristics, such as diameter, aspect ratio, and surface functionalization. Advanced dispersion methods, including sonication and shear mixing, were utilized to ensure even distribution and intercalation of MWCNTs within the matrices. The effect of MWCNTs on the thermal characteristics of the polymer matrix was demonstrated by thermal analysis, which was performed to assess the thermal stability and glass transition temperature (T_g) of the nanocomposites. Additionally, DSC thermograms demonstrate that MWCNT increases T_g. However, pyrolysis of the specified nanocomposite system was expected by TGA for experiments carried out in nitrogen, and nanocomposites in these conditions did not perform any better.

The composite is found to be unchanged by thermal exposure above T_g, so the elastic modulus of the post-cured specimens remains remarkably close to that observed in the virgin specimens at room temperature. The mechanical and DSC results are supported by the DMA study as well. MWCNT has shown to have excellent mechanical and physical properties, and their low density makes it an excellent material for composite reinforcement.

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